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Coherent Anti-Stokes Raman Spectroscopy (CARS) Software Development - Project Report (1991a) for EMR

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1 Introduction

Coherent Anti-Stokes Raman Spectrocopy or CARS is an optical technique valuable for combustion diagnostics. For the past several years Atlantis Scientific has contributed to the deveopment and continuous upgrading of a specialized software package for CARS spectroscopy through contracts sponsored by Energy Mines and Resources (EMR), the National Research Council (NRC) and the Defence Research Establishment Val Cartier (DREV). Information on the CARS technique and the capabilities of the existing CARS software can be found in previous reports (Parameswaran, 1990a) and the references therein.

The present report describes the recent additions and improvements made to the CARS analysis software package under a contract from EMR.

2 Rotational CARS

In the application of CARS spectroscopy to combustion diagnostics usually the populations of vibrational-rotational levels of the molecules are probed to estimate temperatures and species concentration. This method is often referred to as vibrational CARS. Another way of obtaining this information from CARS spectra is to probe the rotational levels. The pure rotational transitions are narrower and more separated (8 cm-1 for N_2) than the rovibrational transitions. This implies that the problem of line overlap and the associated collisional narrowing at high pressure may be neglected for rotational CARS. Rotational transitions also have larger Raman cross sections as compared to vibrational transitions. These characteristics make rotational CARS spectroscopy a viable alternative (Kroll et al. 1990) to vibrational CARS provided experimental problems such as low signal intensity and poor dye laser efficiency are not present. Some of these difficulties have been overcome by the use of excimer laser based CARS systems (Dick and Gierulski 1986) and by using the dual broadband approach (Eckbreth and Anderson 1986; Alden et al. 1986). The dual broadband and conventional rotational CARS methods are compared by Alden et al. (1989).

The resonant susceptility χ_R for rotational CARS can be calculated by a method similar to that outlined for vibrational CARS (Parameswaran and Snelling, 1988) by using the appropriate line strength which in this case is a function of the polarizability anisotropy (Schrotter and Klockner 1979). Summing over all rotational lines,

$$\chi_R(\omega_{as}) = 4\pi(N/h)\frac{\Sigma_J(4/45)\gamma^2 corr(J)^2 B_{JJ'}\Delta_{JJ'}}{(2\delta - i\Gamma_J)} \qquad (1)$$

where ω_{as} is the CARS frequency, N is the number density, h is the Planck's constant, γ is the polarizability anisotropy, corr is the correction for centrifugal distortion, δ is the detuning, Γ is the Raman linewidth and $\Delta_{JJ'}$ is the population factor. The

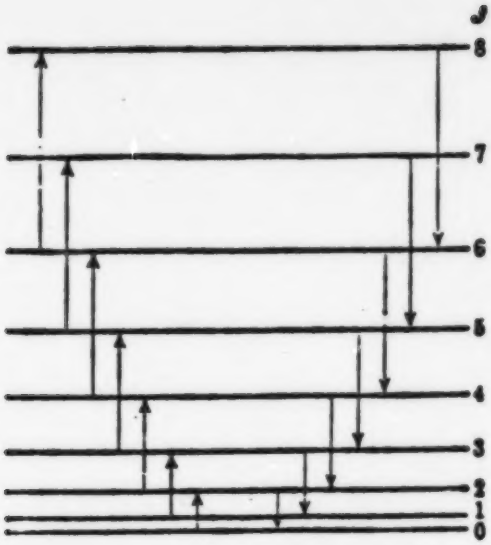

Figure 1: Selection rules for rotational Raman transitions

Placzeck Teller factor $B_{JJ'}$ is given by

$$B_{JJ'} = \frac{3(J+1)(J+2)}{2(3J+1)(2J+3)} \tag{2}$$

and the correction corr is given by (Buckingham and Szabo 1978; Sandia private communication).

$$corr(J) = (\frac{1+(2B_e/\omega_e)^2\gamma' r_e D_{JJ'}}{\gamma})^2 \tag{3}$$

where B_e, ω_e are molecular constants, γ and γ' are the polarizability anisotropy and its deivative with inter nuclear distance given by r_e and

$$D_{JJ'} = J(J+1) + 2J + 3 \tag{4}$$

In the actual calculation it convenient to express polarizability in units of the Bohr radius which is 0.52918E-8 cm. The selection rules for rotational Raman transitions are

$$\Delta J = \pm 2 \tag{5}$$

In this equation ΔJ is defined as $J' - J$ where J and J' are the rotational quantum numbers for the lower and upper levels respectively. Therefore ΔJ is always +2 but two sets of transitions occur depending on where they originate as shown in Figure.1 (Herzberg, 1963). To enable the EMR laboratories to generate and analyze rotational CARS spectra the necessary theory was implemented in the CARS software package. In particular the theoretical spectrum generating program SPT_GENERATE was modified to calculate the amplitudes of pure rotational transitions. Appropriate

Placzek factors and centrifugal distortion correction factors were introduced in calculating the line strengths. A typical rotational CARS spectrum of pure nitrogen at a temperature of 1850 K and at atmospheric pressure, over a 50 cm^{-1} region is shown in Figure.2 where the spectrum N_ROT is obtained from the GENERATE program and S_ROT is from the Sandia program. The isolated line model with K-T convolution (IT), and a pump width 1.8 cm^{-1} were used. The symbols in the spectral plots are explained in the User manual for the plotting program (Friend and Parameswaran 1991). The two spectra agree closely and the lower A-B plot shows only small negligible differences. In Figure.3 the 1300 K rotational CARS spectrum of nitrogen over a larger wavenumber region (pump width = 0.67 cm^{-1}) is displayed. This spectrum is similar to that shown in Alden et al.'s work. When experimental data becomes available at EMR more detailed comparisons can be made. Rotational CARS spectra for a molecule can be calculated as described in the User manual for the program SPT_GENERATE (Parameswaran, 1991b) by using the appropriate frequency limits STRT_FREQ and FIN_FREQ in the input data file.

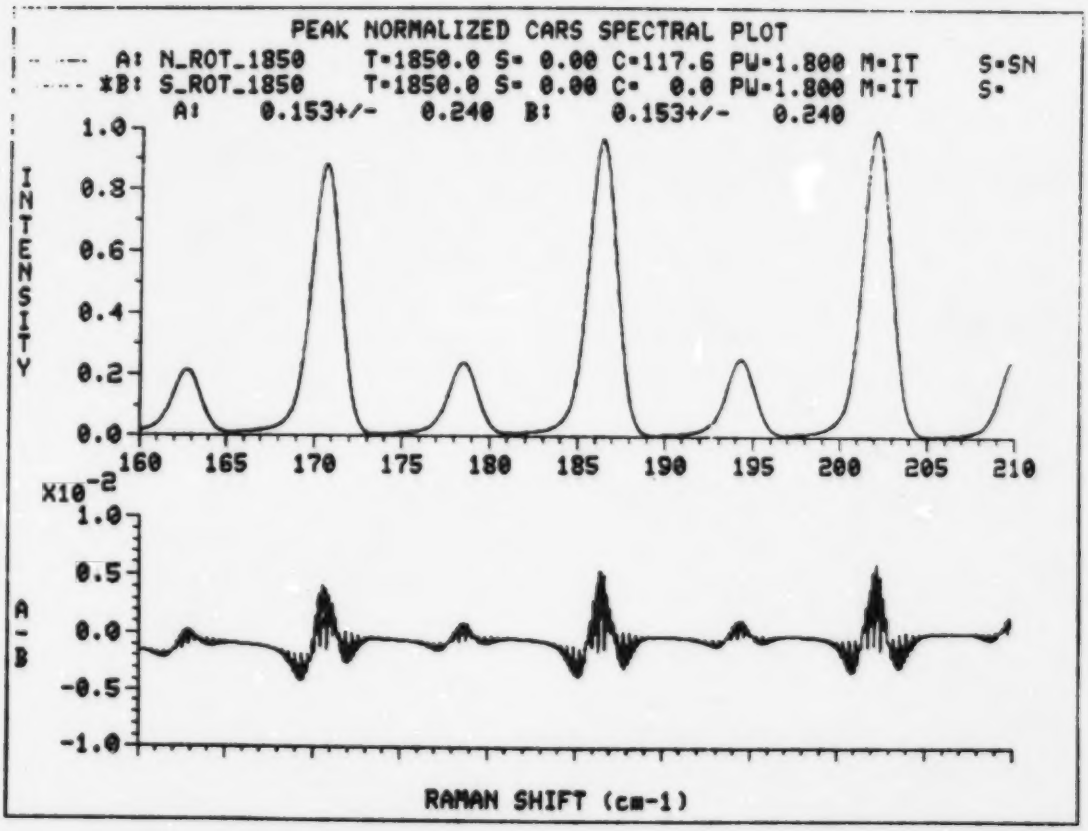

Figure 2: Comparison of pump convolved N_2 rotational CARS spectra from GENERATE and Sandia codes

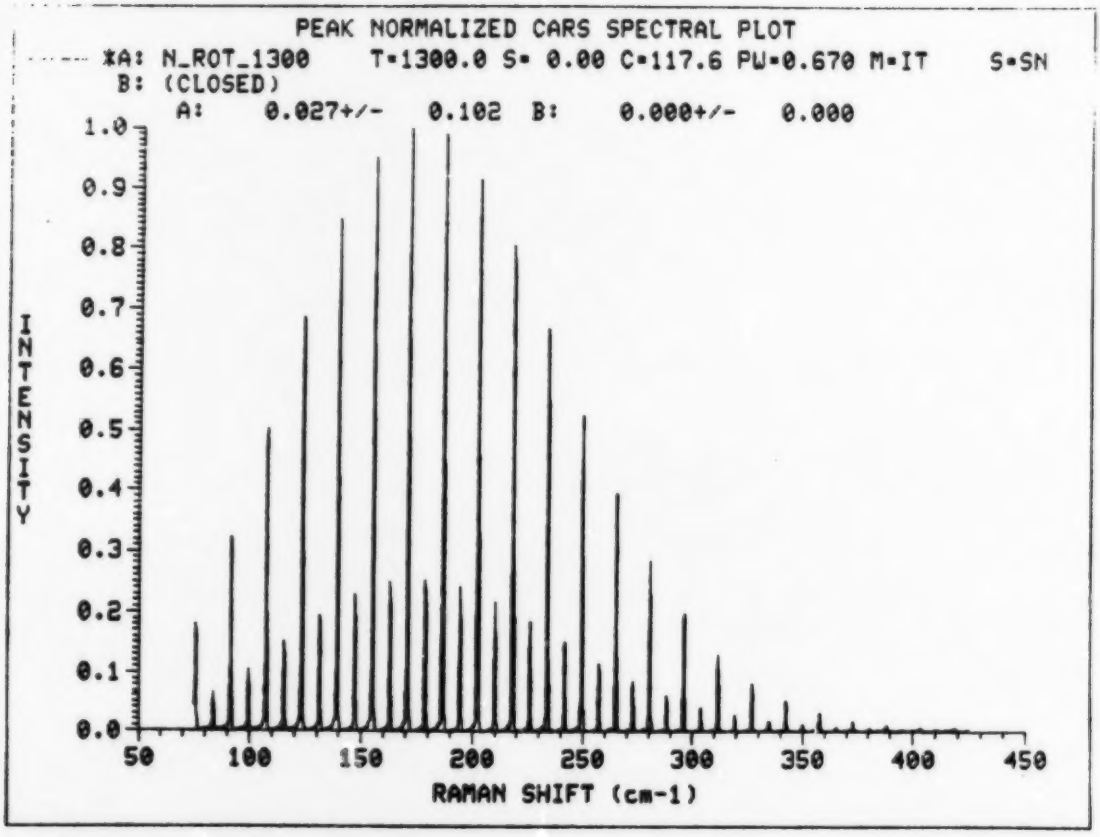

Figure 3: Pump convolved N_2 rotational CARS at 1300 K

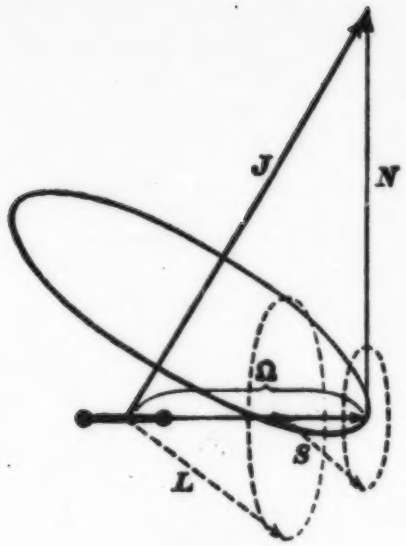

Figure 4: Vector Diagram for Hund's case (a) as in NO

3 The theoretical CARS spectra of the NO molecule

Nitric oxide (NO) is a diatomic molecule which can be present in coal combustion. A literature study of this molecule was undertaken with respect to its spectroscopic properties and the following information was gathered. At the outset it might appear that the calculation of the CARS spectrum of NO should be straight forward once its molecular constants and other necessary input parameters are known. However NO has a rather complex Raman spectrum because of its electronic ground configuration which is a π^2 state and has a nonzero orbital angular momentum L = 1 of electrons along the internuclear axis. In a molecule, the electronic orbital angular momentum **L**, the electron spin **S** and the angular momentum of nuclear rotation **N** combine to form the total angular momentum **J**. If **L** and **S** are zero then the molecule has a Σ^1 state and **J** equals **N**.

When this is not true the resultant level structure and spectra depend on the relative coupling betwen **L**, **S** and **N** as indicated by Hund's rules. In Hund's case(a) it is assumed that the coupling of electronic orbital and spin angular momenta with nuclear motion is weak but the electronic motion is very strongly coupled to the internuclear axis. Thus **L** and **S** first couple to form a resultant vector Ω which then combines with **N** to form the total **J** as shown Figure.4 (Herzberg 1963). In this figure Ω and **N** nutate about **J** while **L** and **S** precess about the internuclear axis. In NO, L = 1 with component of orbital angular momentum along the inter nuclear axis $M_L = \pm 1$ and component of spin angular momentum along the inter nuclear axis $M_S = \pm 1/2$. The total electronic angular momentum Ω can have values 1/2 or 3/2 giving rise to two states split by spin orbit interaction by about 124 cm^{-1}.

These electronic angular momenta further combine with the nuclear rotation to give the total angular momentum J of the molecule for each state. The double degeneracy of these states due to the $\pm$ values of M_L is often referred to as lambda doubling. In Hund's case (a) the coupling between electronic motion and nuclear rotation is neglected. As the speed of rotation increases with J, this coupling comes into effect and causes a small splitting (fraction of a cm^{-1} of the above doublets.

The Raman spectrum of NO consists of two overlapping Q branches from each of the Ω branches of the ground state. The degree of overlap of the Q branches is different for different values of J. For example the J = 3/2, Ω = 3/2 transition overlaps completely with the J=7/2, Ω = 1/2 transition. There can also occur transitions between levels with different values of Ω. In simulating the CARS spectrum of NO it is important to sum over the two Q branches while taking proper account of the above overlapping transitions. Further, correct transition frequencies should be determined with proper molecular constants and the appropriate approximation for the coupling between electronic and nuclear motions. The complexity of the vibration rotation bands of NO is discussed by Valentin et al. 1978 and Amiot et al. (1977). Lempert et al.(1984) have studied the collisional narrowing in NO Q branch and provide relaxation rate matrix elements obtained from stimulated Raman spectroscopy. Interference effects arising from pressure broadening in NO are also investigated by Laane and Kiefer (1980).

Thus the existing theoretical CARS generating program will require major modifications and/or additional routines to be applicable for NO. The relevant background study has been done and the program modification will be undertaken in future work.

4 Updating of molecular data

Recent publications on CARS as well as the molecular constants of the species N_2, CO, O_2, H_2, H_2O, and CO_2 were examined from time to time. It was ensured that the latest information available on these molecules was incorporated in setting up the input data files used for generating their theoretical CARS spectra. Typical input data files for all the above molecules are given in the appendix of the User Manual for SPT_GENERATE (Parameswaran, 1991b).

5 Modifications to the program SPT_FIT

5.1 Multiple frequency regions for the fit

The program SPT_FIT can yield best fit values of temperature, frequency shift, concentration and slit parameters by comparing experimental CARS spectra with the-

oretically calculated spectra. In analyzing CARS spectra from coal burning flames it is desirable to do the fit over a certain selected frequency range. To facilitate this the fitting program was modified to have the option of fitting over one, two or three ranges of frequencies. This modification involved changes to the program SPT_FIT and some of the subroutines it calls. This feature is useful in excluding an intermdiate region, in the total fit range, which may contain spurius structure making the fitting process difficult.

5.2 User friendly input for SPT_FIT

In the previous versions of the fit programs some of the input data is obtained from the user interactively during each analysis. Since this program accepts several input variables this method can be sometimes be cumbersome. To speed up the acquiring of input data a method of entering only those input parameters that have changed since the last run, was devised. This was achieved by setting up a text file which stores all the input variables along with clear descriptions. This file can be easily edited before each analysis. The user may also change any of the 44 variables interactively when SPT_FIT starts execution and update the existing input data file called FITDATA.DAT. Input/output from this file is made possible by subroutines designed and added for this purpose.

The modified version of this program and examples showing the use of FITDATA.DAT are given in the User Manual for SPT_FIT (Parameswaran, 1991c).

6 The program SPT_TRANS_THEORY

The CARS fitting and plotting programs are designed to read only binary spectral files with .SPT extensions. These binary files cannot be directly edited but can be indirectly viewed with the help of the SPT_REPORTER program. The program SPT_EDITOR also allows one to edit some parts of .SPT spectral file. Often it is desirable to be able to directly edit the spectral files. To satisfy this requirement s computer program called SPT_TRANS_THEORY for converting .DAT type ascii files of thoretical CARS spectra to .SPT type binary files and to convert binary files to ascii files was developed. This program is also useful in converting ascii files calculated in the PC computer and transferred to the VAX computer. The two computers store binary data differently due to the difference in their architecture and hence binary files cannot be directly transferred from the PC to the VAX and compared with VAX generated files. Such a comparison is necessary to test CARS programs ported from the VAX to the PC as described in the next section.

In future work, there are plans to modify this program to also translate experimental CARS spectral files and to write a User manual to document its features.

7 Porting of the program SPT_GENERATE

The program SPT_GENERATE, and the programs in the libraries THRYLIB, SPTLIB were copied from the VAX to the PC computer. Compilation of some of these programs with MS FORTRAN and NDP FORTRAN was tested. The SPT_GENERATE program and its subroutines were compiled with NDP FORTRAN version 2.1 and initial test runs were made. In this conversion process VAX system dependent functions and subroutines had to be suppressed or replaced by equivalent available counterparts in NDP FORTRAN. These are preliminary changes and more modifications may be required to make the PC versions more efficient and robust.

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